

Investigation on the Platinum-Loaded NaY Zeolite Catalysts for Liquid Phase Reforming of Carbohydrates to Hydrogen

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ABSTRACT

Hydrogen production from biomass has been paid more attention for years. Processes suggested for production of hydrogen from biomass are often involved in high-temperature pyrolysis^[1-2], catalytic steam reforming^[3] or enzymatic biosynthesis^[4]. These strategies, however, encounter problems of high consumption of energy, low catalyst efficiency and very limited productivity. Group VIII metals such as Pt, Ni and Ru are more likely to be effective catalysts for reforming of oxygenated hydrocarbons (the main component in biomass), and among which, only Pt and Pd show both high activities and high selectivity for production of H₂^[5-7]. Although lots of catalysts have been screened for this aqueous-phase reforming, the catalysts with high loadings noble metal such as platinum has to be used even when conducting at low feed concentration of 1 wt%^[8]. Therefore, highly active catalytic materials need to be developed in order to render the process practical.

In this work, platinum aggregates encaged in Y-type zeolite were prepared by ion-exchange of the NaY zeolite in tetra-amine platinum nitrate solution followed by calcination and reduction. Micropore BET & Chemisorption Analyzer with computer workstation was used to measure the BET area surface, pore volume of the catalysts. Chemisorption of carbon monoxide shows that the CO-uptake of platinum on the Y zeolite is between 8.8 and 11.8 μmol/g cat, according to the ion-exchange procedure and the conditions of pretreatment. The Cameca SX-100 Microprobe equipped with 3 wavelength dispersive (WD) spectrometers, plus secondary electron and high-speed backscattered electron detectors was used to conduct quantitative analyses on individually selected points or point grids, so that the metal content on the support can be calculated.

Experiments were carried out in a fixed-bed reactor system. The catalytic performance of the Pt/NaY catalysts was evaluated and compared with the state-of-the-art Pt/γ-Al₂O₃ catalysts. The Pt/NaY catalyst with a Pt loading of 0.5wt% exhibited catalytic performance comparable to or better than the Pt/γ-Al₂O₃ with a Pt loading of 2.9wt% in liquid phase reforming of methanol solutions at 493~538 K.

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The as-synthesized PtY catalysts have shown good activity for hydrogen production by aqueous reforming from some biomass derived oxygenate compounds. The aqueous-phase reforming reactions of methanol and ethanol were carried out under the conditions of 498 K, 2.81 Mpa and 538 K, 5.51 Mpa over PtY catalysts and Pt/ γ -Al₂O₃ catalysts. It has been shown that the activities of the employed catalysts decrease as the platinum loadings on the support decrease.

The experimental results of liquid phase reforming of methanol over our best two catalysts (namely, 3% Pt/ γ -Al₂O₃ and 0.5 wt% PtY) are shown in Table 1, some of which are compared with the data from literature^[8]. It should be noted that the conversion of methanol over 3% Pt/ γ -Al₂O₃ catalyst at 498 K is lower than that in the literature probably because the surface area (259.3 m²/g) of Al₂O₃ synthesized in this work is much lower than the surface area of the nanofibers of γ -Al₂O₃ (500 m²/g). The results of conversion over 0.5 wt% PtY catalyst show that the conversion of methanol decreases with the temperature. Turnover frequencies (TOF) were calculated from the rates of hydrogen production and then normalized by the number of surface metal atoms as determined from irreversible uptake of CO at 308K. It can be seen from the Table 1 that TOF of 0.5 wt% PtY catalyst is approximately 6 times higher than the TOF of 3% Pt/ γ -Al₂O₃ catalyst. Table 1 also shows that the performance of 0.5 wt% PtY catalyst is better than that of 3%Pt/ γ -Al₂O₃ (with Pt loading of about 2.9 wt.%) when carried out under the investigated reaction conditions.

Table 1 Comparison of data between 3%Pt/Al₂O₃ and 0.5 wt% PtNaY catalysts

	Reference ^[7]		3%Pt/Al ₂ O ₃		0.5 wt%-PtY	
			120 h	120 h	120 h	120 h
T/K	498	538	498	538	498	538
P/MPa	2.86	5.53	2.81	5.51	2.81	5.51
C in Liquid, %	6.5	6.4	19.5	4.8	18.6	0.8
Conversion, %	94	94	78.9	95.5	81.0	98.8
Gas Product						
H ₂ (mol,%)	74.6	74.8	74.6	74.5	74.6	74.4
CO ₂ (mol,%)	25.0	24.6	24.9	24.9	24.8	24.8
CH ₄ (mol,%)	0.4	0.6	0.5	0.6	0.6	0.8
H ₂ Selectivity, % ^[a]	99	99	97.6	97.1	97.1	95.6
Alk Selectivity, % ^[b]	1.7	2.7	2.0	2.4	2.4	3.0
Rate of H ₂ Production ^[c] /(mmol.g ⁻¹ .h ⁻¹)	0.70	0.70	0.57	0.71	0.58	0.74
TOF /min ⁻¹	0.16	0.16	0.16 ^[d]	0.20 ^[d]	0.82 ^[d]	1.04 ^[d]

[a] Based on H-balance, selectivity of hydrogen = H₂/(H₂+4×CH₄). [b] Based on C-balance, selectivity of alkane = CH₄/(CH₄+CO₂). [c] WHSV=0.008g of methanol per gram of catalyst per hour. [d] Normalized by the number of surface metal atoms as determined from irreversible uptake of CO at 308K.

98.8% conversion of methanol and 95.6% selectivity to hydrogen have been achieved at 538 K, 5.51 Mpa over 0.5 wt% PtY catalyst which are even better than the results from Pt/

γ -Al₂O₃ catalysts with 2.98 wt% platinum loading. When ethanol was used as feedstock at the same condition, the conversion of ethanol and the selectivity to hydrogen were 68.3% and 94.8%, respectively (Table 2). However, the rate of hydrogen production (0.79 mmol.g⁻¹.h⁻¹ at 538K, 5.51MPa) with ethanol as feedstock (WHSV = 0.008g, i.e. feed rate = 0.174 mmol of ethanol per gram of catalyst per hour) is even higher than that of methanol (0.74 mmol.g⁻¹.h⁻¹ at 538K, 5.51MPa, WHSV = 0.008g, i.e. feed rate = 0.25 mmol of methanol per gram of catalyst per hour) because one mole of ethanol can generate six mole hydrogen, while one mole methanol can only generate three mole hydrogen.

Table 2 Experimental data for reforming of ethanol over 0.5 wt% PtY catalyst

T/K	498	518	538
P/MPa	2.81	3.88	5.53
Conversion, %	59.6	65.7	68.3
Gas Product			
H ₂ (mol,%)	73.9	74.1	74.1
CO ₂ (mol,%)	24.6	24.7	24.7
CH ₄ (mol,%)	1.2	1.0	1.0
C ₂ H ₆ (mol,%)	0.3	0.2	0.2
H ₂ Selectivity, % ^[a]	94.0	95.2	94.8
Alk Selectivity, % ^[b]	5.7	4.6	4.6
Rate of H ₂ Production ^[c] /(mmol.g ⁻¹ .h ⁻¹)	0.62	0.70	0.79
TOF ^[d] / min ⁻¹	0.88	0.99	1.10

[a] Based on H-balance, selectivity of hydrogen = H₂/(H₂+4×CH₄+C₂H₆). [b] Based on C-balance, alkane selectivity = (CH₄+C₂H₆)/(CH₄+2×C₂H₆+CO₂). [c] WHSV=0.008g of ethanol per gram of catalyst per hour. [d] Normalized by the number of surface metal atoms as determined from uptake of CO at 308K.

Longevity test has shown that both the PtY and Pt/ γ -Al₂O₃ catalysts have good stability when used in aqueous-phase reforming reaction. The activity of PtY catalysts is much higher than that of the Pt/ γ -Al₂O₃ catalysts with same platinum loading indicating that PtY catalyst might be a promising cost effective catalyst for hydrogen production from biomass.

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